

The Sonic Interferometer.
The Velocity of Sound in Some Organic
Liquids and in Solutions of Certain
Alkali Halides

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
EGBERT BARROWS FREYER
Baltimore, 1928

EASTON, PA.:
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SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS.

I. THE SONIC INTERFEROMETER. THE VELOCITY OF SOUND IN SOME ORGANIC LIQUIDS AND THEIR COMPRESSIBILITIES

A number of investigators¹ have studied the velocity of sound in liquids at audible frequencies but the methods are beset with so many difficulties and involve the use of such large quantities of liquids that few results of adequate precision for thermodynamic treatment have been obtained. More recently² the field of high frequency sound production using piezo-electric crystals has been entered, and Hubbard and Loomis³ have developed a method which has yielded very accurate values for the velocity of sound in liquids. The investigation recorded here was conducted according to their method and is a part of the general program of thermodynamic research on organic compounds now being undertaken at this Laboratory. The sonic interferometer has been further developed with especial reference to temperature control, the prevention of evaporation of the liquid being studied and of contamination by water vapor from the air.

Apparatus and Method

The electrical equipment is shown in Figs. 1, 2 and 3. When the circuit Y is tuned by means of the condenser (15), a heterodyne is produced between the two oscillating circuits. When the note is made to coincide in pitch with that produced by the tuning fork, the crystal in the interferometer is known to be vibrating with the same frequency

¹ Schmidt, *Wiener Ber.*, (IIa) **114**, 945 (1905); Dörsing, "Inaug. Diss.," Bonn, 1907; *Ann. Physik*, [4] **25**, 227 (1908); Busse, *ibid.*, **75**, 657 (1924); Pooler, *Phys. Rev.*, **31**, 157 (1928) (abstract).

² Boyle, *Trans. Roy. Soc. Canada*, **17**, 141 (1923); 159, 191, 197 (1925); 79 (1927); Langevin, British Patent Spec. N. S. 457, No. 145,691 (1920).

³ Hubbard and Loomis, *Nature*, **120**, 189 (1927); *Phys. Rev.*, **31**, 158 (1928); *Phil. Mag.*, VII, **5**, 1177 (1928).

as circuit X⁴ (this being fixed and determined by crystal (7)), plus or minus 1000 cycles, the frequency of the fork. Exact coincidence of the two audible frequencies is indicated by the disappearance of the easily discernible beats heard when the fork is operated.

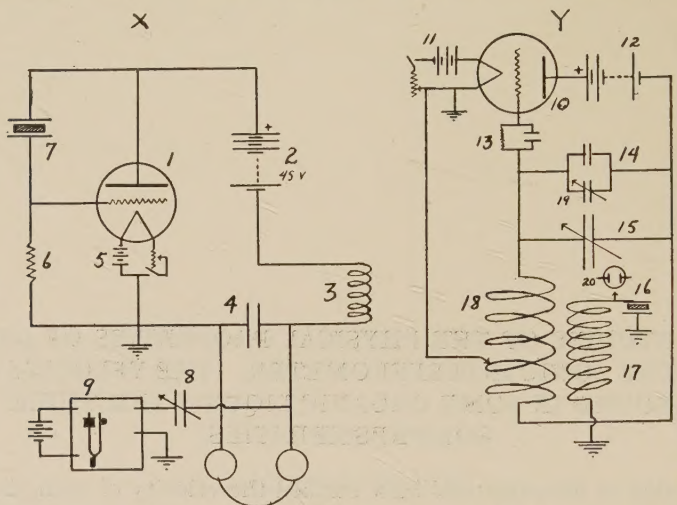


Fig. 1.—X. *The Pierce Oscillator*: 1, UX, 199 tube; 2, 45 volts; 3, choke, 30 millihenries; 4, 0.002 mf.; 5, two dry cells in series; 6, grid leak, 1 megohm; 7, crystal, see Fig. 2; 8, 0.0005 mf.; 9, 1000-cycle electrically driven tuning fork (General Radio). Y. *The Hartley Oscillator*: 10, UX-171 or UX-210 tube; 11, 7 volts, D. C.; 12, 180 to 300 volts D. C.; 13, grid leak, 1 megohm; 0.002 mf.; 14, 1 to 3 mf. (so arranged that 1, 2 or 3 mf. may be used); 15, 0.001 mf.; 16, sonic interferometer, see Fig. 3; 17, 60 to 90 turns of No. 25 B. and S. insulated copper wire, wound closely, diameter of coil, 4"; 18, 30 turns of No. 16 B. and S. bare copper wire, coil 5" in diameter, 6" long, alternate turns provided with projections to clip onto; 19, two plate vernier condenser; 20, neon lamp, see Fig. 4.

The final tuning is effected by means of the vernier condenser. Assuming the lower surface of the interferometer piston to be in a nodal plane, *i. e.*, assuming a system of

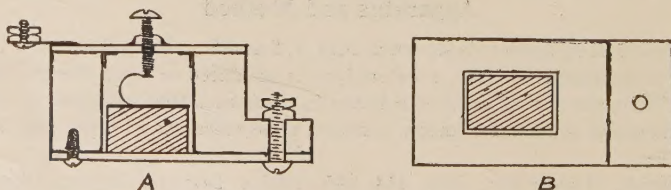


Fig. 2.—Housing for control crystal (7) in Fig. 1.

"stationary waves" in the liquid, the beats will return if the piston is raised or lowered even a very slight distance (0.002 mm.). By a proper simultaneous manipulation of

⁴G. W. Pierce, *Proc. Am. Acad.*, 60, 269 (1925). For other circuits see *Proc. Inst. Radio Eng.*, 15, 9 (1927).

the vernier condenser and the micrometer screw on the interferometer the nodes are located and their relative positions read from the micrometer screw scale. A reading of the screw setting is taken when the beat frequency is zero (piston in node); calling this reading x , and lowering the piston through the liquid for a distance of about two centimeters, counting meanwhile the number of nodes, n , a second screw reading, y , is taken for the position of another node. Then $(x - y)/n = \lambda/2$ and $2\omega \times (x - y)/n = v$, where ω is the frequency of oscillator Y, and v is the velocity of sound in the liquid.

The accompanying drawings illustrate the essential details of the apparatus. Brief mention may be made of the experimental arrangement.

The circuits were mounted on a board bearing a hard rubber panel supporting the condensers and rheostats; this was in turn mounted in a copper-lined box for shielding. The control dials were placed on the outside of this box to be within easy reach. As measurements were made in a number of different thermostats, the entire apparatus was made portable. The box was screwed to the top of a table mounted on rubber-tired casters. Several inches from the floor was a large shelf supported by the table legs; this carried all of the batteries. These and the leads to the circuits above them were shielded by enclosing the whole in copper window screening, using the table to support this. The wire leading from the secondary coil to the sonic interferometer was shielded by running it through a brass tube three centimeters in diameter by thirty centimeters long. It was attached to the side of the box through a universal joint. The lead was maintained rigid in the tube by having it pass through a glass tube supported at either end by corks. As there was a considerable potential between this wire and the shielding (about 1000 volts if a UX 210 tube is used), a pronounced condenser action resulted between the two; to keep this at a minimum, the lead was as short as possible and not too close to its shielding. Contact with the interferometer was made by a clip on the same, the contact itself being shielded by a sheath which slid over the brass tube bearing the lead.

An alternate, though less precise, method of detecting the nodes involves the use of a neon lamp (20). This was mounted in a tube as shown in Fig. 4; whenever the circuit was oscillating, the lamp exhibited a red glow. When the piston was exactly in a node, however, the glow either disappeared entirely (owing to the drop in the value of the current) or so changed in shape and intensity that there was no mistaking the

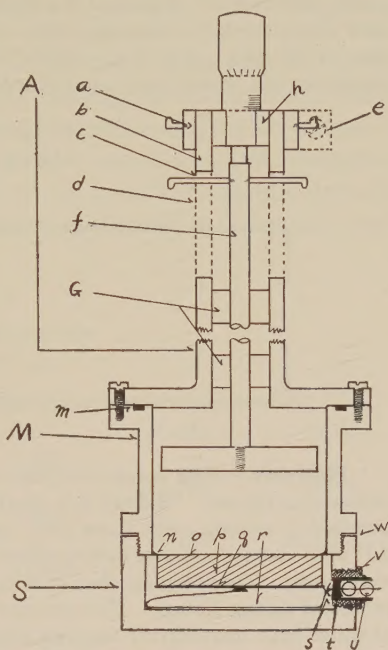


Fig. 3.—The Sonic Interferometer: Materials: A, bronze; M, iron; S, bakelite; f, "Invar" steel; a, e, clamp; b, four vertical slots, not shown; c, hook for rubber bands; d, slot; g, guide collars; m, rubber gasket, slightly thicker than depth of groove; n, solder; o, phospho-bronze, 0.005" thick; p, quartz disk; q, bronze or brass; r, spring; s, good contact; t, deKhotinsky; u, glass beads; v, brass bushing into which is soldered the copper tube bearing the lead wire; w, water-tight seal. The piston and inside of the cup were gold plated.

position of the node as read on the micrometer screw. Even when this device was not used for the precise determination of the separation of the nodes, it very conveniently served as an indication of when the circuit was oscillating. The character of the glow was determined by the distance between strip (a) and the lamp. Cemented to the screw was a glass tube to insulate the high tension wire against the hand when adjustments were made. In general, for detecting nodes, the distance (a) was such that the glow was quite faint when the piston was *not* in a node. The lens rendered a better view of the glow. The device was mounted by a universal joint to the top of the box containing the circuits and could thus be made visible from any angle.

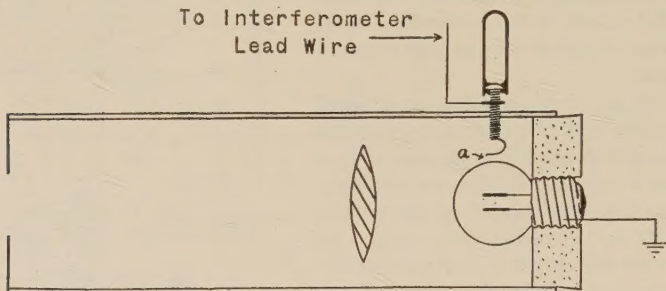


Fig. 4.

Materials.—With a few exceptions the samples studied in this investigation were prepared as follows: "Baker's C. P. Analysed" liquids were distilled through a three-foot punched-in column, only those cuts being taken for measurement that boiled within 0.1° of the latest published boiling points. Appropriate barometric and stem corrections were made. Those liquids that tend to dissolve water vapor were carefully dried and protected during storage. The glycerin (Baker's Analysed) was dried for several hours at water-bath temperature through phosphorus pentoxide. The purity of the bromoform and α -bromonaphthalene was questionable, but these liquids were included in the investigation only because they, like benzene, melt at a convenient temperature and it was desired to ascertain if the break in the velocity of the sound-temperature curve, noticed first in the case of benzene, was a phenomenon of general occurrence. The isomeric heptanes were prepared in the research laboratory of the Ethyl Gasoline Corporation and kindly loaned to us for use in this investigation.

Sources of Error and the Precision.—A possible source of error was the absorption of water vapor from the air during the actual measurement. This apparently was quite appreciable in the case of acetone, as manifested by the difference between two readings made an hour and a half apart. It was avoided by using a fresh sample of the liquid for each measurement. This error was borne in mind throughout the investigation and appropriate precautions were taken to avoid it. A new design of the spring mechanism on the piston entirely eliminates this source of error by closing up the slots (d).

For some reason not yet ascertained the oscillations were considerably weakened at temperatures above 50° and with some liquids they disappeared entirely. The values given for the velocity of sound at this temperature are extrapolated ones. If an air bubble is entrapped under the piston

when it is inserted, the sonic "reaction" may be greatly weakened or entirely absent.

As a rule screw readings were taken on three or four adjacent nodes when the piston was near the upper limit of its range and three or four when it was near the lower limit, the number of nodes in the interval being, of course, known. Occasionally, however, the position of each node was determined, as sometimes the $\lambda/2$ value between two nodes near the center of the liquid column would be a freak one, differing for no apparent reason from all of the others. Such a value was ignored in averaging the values of $\lambda/2$. It is felt that this procedure was justified, considering the close agreement between all of the normal values and the great discrepancy between the normal ones and the "freak" datum, as illustrated in a sample determination shown in Table I.

TABLE I
SAMPLE DETERMINATION
Alcohol at 20° (A)

Screw reading, x mm.	Diff. = $\lambda/2$	Screw reading, y mm.	Diff. = $\lambda/2$	$x - y$	$\frac{x - y}{n} = \frac{\lambda}{2}$
18.085		6.590		11.495	1.4370
	1.440		1.445		
16.645		5.145		11.500	1.4375
	1.440		1.440		
15.205		3.705		11.500	1.4375
	1.440		1.440		
13.765		2.265		11.500	1.4375

$$V = 2 \frac{\lambda}{2} \omega = 1168 \text{ m./sec.}$$

Benzene at 35° (B)

Screw reading	19.460	17.910	16.365	14.814	13.270	11.722
Difference		1.550	1.545	1.551	1.544	1.548
Screw reading	11.722	10.175	8.625	7.105	5.553	4.008
Difference		1.547	1.550	(1.520)	1.552	1.545

Mean difference, 1.548. $V = 1254 \text{ m./sec.}$

As the data in the last column of (A) represent a precision greater than could be attained using different samples of a liquid, only four significant figures are retained for the most part in the final value of the velocity of sound. Usually independent measurements gave results that checked to one meter per second. The velocity of sound in water, for example, was found on two different occasions to be 1498.6 and 1498.3 m./sec. The average of a large number of determinations by Hubbard and Loomis with a different interferometer and at a different frequency gave 1498.1. The former figures were obtained without making any special effort to attain the maximum precision of which the method is capable.

Mention should be made of the behavior of the frequency control crystal

during these measurements. The crystal and its principal frequency calibration was furnished by the Naval Research Laboratory. In addition to the principal frequency, the crystal exhibited others, as is usually the case: a parallelepipedal oscillator may vibrate along three axes under proper circumstances, each of these periods may have overtones and the crystal may also oscillate with a period which results from the coupling of vibration of two of these modes. When these "overtones" are present they are quite definite and sharp (but easily distinguishable from the fundamental by the character of the audible heterodyne note). At one time, however, the constants of the circuit were such that abrupt changes in frequency occurred, the crystal vibrating now in one, now in the other, fundamental frequency. A careful check showed which liquids had been measured on the new frequency and its value was established in the following manner. Six careful determinations of the wave length in several different samples of pure, air-free distilled water were made. From the accurately known values of the velocity of sound in water at the temperatures of measurement⁵ the frequency was calculated. The velocity of sound values used were taken from a curve drawn through a large number of points (about 50) in a 40° temperature interval. They are believed to be accurate to one part in ten thousand. The values of the frequency thus found are as follows: 414.0, 414.1, 414.3, 414.1, 413.8, 413.8—mean, 414.0(1) kilocycles.

These were checked to about 1% with a wavemeter, and, further, at different intervals of time by other sound wave-length determinations. The definiteness and constancy of the new frequency was thus firmly established.

Results and Calculations.—In the following tables are given the

TABLE II
VALUES OF THE ISOTHERMAL COMPRESSIBILITY AND C_p/C_v CALCULATED FROM THE VELOCITY OF SOUND, ETC.

Temp., °C.	Vel. of sound m./sec.	ρ	dv/dT	C_p	$\beta_T, \text{atm.}^{-1}$ $\times 10^6$	C_p/C_v	$\beta\phi \times 10^6$ Tyrrer	$B\phi$ (F., H. and A.) $\text{Atm.}^{-1} \times 10^6$
Benzene								
0		0.9001	0.00131	0.3970			56.6	
10	1375	.8896	.00134	.4027	87.5	1.449	61.3	60.3
20	1324	.8790	.00138	.4084	94.9	1.441	66.3	65.8
30	1278	.8684	.00142	.4141	102.5	1.435	71.7	71.5
40	1231	.8576	.00146	.4196	111.0	1.422	77.8	78.0
50	1184	.8467	.00151	.4255	119.9	1.420	84.6	85.4
Alcohol								
0	1242	0.8062	0.001286	0.5487	97.6	1.196	83.5	81.5
10	1204	.7978	.001325	.5706	104.4	1.191	89.8	87.6
20	1168	.7893	.001370	.5950	111.3	1.183	95.7	94.1
30	1134	.7809	.001420	.6208	119.6	1.184	102.0	101.0
40	1101	.7722	.001475	.6478	127.8	1.181	109.0	108.2
50	1067	.7632	.001550	.6762	137.8	1.182	116.7	116.6

TABLE II (Continued)

Temp., °C.	Vel. of sound m./sec.	ρ	dv/dT	C_p	$\beta_T, \text{atm.}^{-1} \times 10^8$	C_p/C_v	$\beta_\phi \times 10^8$ Tyrer	B_ϕ (F., H. and A.) $\text{Atm.}^{-1} \times 10^8$
Acetone								
0	1273	0.8125			...	...	...	77.0
10	1231	.8014			...	...	...	83.5
20	1190	.7905	0.001881	0.514	129.2	1.426	...	90.6
30	1146	.7788			...	...	...	99.1
40	1102	.7672	0.002122	.530	158.2	1.456	...	108.8
50	1057	.7554			...	...	...	120.1
Chlorobenzene								
0	1362.5	0.8666	0.000850		...	...	49.05	47.3
10	1322.5	.8952	.000867		...	...	52.30	51.9
20	1284.5	.9040	.000880	0.315	74.8	1.348	55.7	55.5
30	1248.0	.9129	.000895	.322	79.4	1.338	59.4	59.4
40	1212.5	.9220	.000910	.328	84.3	1.325	63.4	63.6
50	1178.0	.9309	.000925	.335	89.5	1.316	67.8	68.0
Toluene								
0	1414	0.8848	0.00124	0.3834	80.8	1.410	59.6	57.3
10	1370.5	.8752	.00125	.3938	85.5	1.388	62.9	61.6
20	1327.5	.8657	.00126	.4042	90.6	1.364	67.4	66.4
30	1284.5	.8563	.00127	.4147	96.2	1.340	72.3	71.8
40	1242	.8470	.00129	.4251	102.7	1.323	77.4	77.6
50	1199	.8378	.00132	.4355	110.4	1.311	83.2	84.2
Chloroform								
0	1069.0	1.5264	0.000810	0.2323	86.6	1.490	58.8	58.1
10	1036.5	1.5078	.000830	.2333	93.1	1.487	63.4	62.6
20	1002.5	1.4888	.000855	.2343	100.7	1.485	68.3	67.8
30	967.5	1.4697	.000884	.2353	109.5	1.486	73.5	73.7
40	932.5	1.4505	.000917	.2363	119.5	1.486	79.4	80.4
50	897.0	1.4310			...	...	...	...
Ether								
0	1095	0.7362	0.00203	0.5290	152.7	1.330	114.5	114.8
10	1054	.7248	.002115	.5349	167.4	1.330	127.5	125.8
20	1006	.7135	.002245	.5527	186.8	1.329	141.0	140.6
30	949	.7019	.002390	.5645	210.8	1.328	156.0	158.7
Carbon Tetrachloride								
0	1008	1.6327	0.000730	.2010	89.7	1.468	62.8	61.1
10	970	1.6134	.000742	.2013	97.0	1.452	67.4	66.8
20	935	1.5939	.000756	.2016	104.8	1.439	72.5	72.8
30	904	1.5748	.000777	.2019	113.3	1.437	78.1	78.8
40	873.5	1.5557	.000805	.2022	123.2	1.433	84.2	85.4
50	843	1.5361	.000837	.2025	134.4	1.427	91.1	92.9
Carbon Disulfide								
0	1223.5	1.2931	0.000880	0.2352	80.5	1.536	52.9	52.4
10	1190.5	1.2783	.000908	.2368	86.5	1.544	56.3	56.0
20	1158.0	1.2634	.000941	.2385	93.1	1.556	60.0	59.8

TABLE II (Concluded)

Temp., °C.	Vel. of sound m./sec.	ρ	$d\rho/dT$	C_p	$\beta T, \text{atm.}^{-1} \times 10^4$	C_p/C_v	$\beta\phi \times 10^4$ Tyrer	B_ϕ (F., H. and A.) $\text{Atm.}^{-1} \times 10^4$
30	1126.0	1.2483	.000983	.2401	100.9	1.574	63.8	64.1
40	1093.5	1.2327	.001036	.2417	110.3	1.603	68.4	68.8
50	1061.0	1.2168	.001097	.2433	121.1	1.636	73.9	74.0

Methyl Alcohol

0	1187	0.8100	0.001468	0.563	109.2	1.230	...	88.8
10	1154	.8007	.001505	.594	116.0	1.221	...	95.1
20	1121	.7913	.001554	.632	123.4	1.211	...	101.9
30	1088	.7818	.001609	.679	131.5	1.199	...	109.6
40	1056	.7723	.001670	.732	140.0	1.189	...	117.7
50	1023.5	.7627	.001741	.793	149.6	1.180	...	126.8

Temp., °C.	Vel. of sound, m./sec.	ρ	B_ϕ (F., H. and A.) $\text{atm.}^{-1} \times 10^4$	Temp., °C.	Vel. of sound, m./sec.	ρ	B_ϕ (F., H. and A.) $\text{atm.}^{-1} \times 10^4$
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Heptane

0	1235	0.7005	94.9
10	1196	.6920	102.4
20	1154	.6836	111.4
30	1112	.6751	121.4
40	1070	.6665	132.8
50	1028	.6579	145.8

 α -Bromonaphthalene

10	1402	1.503	34.3
20	1372	1.487	36.2
30	1341	1.472	38.3
40	1311	1.459	40.4
50	1280	1.448	42.7

Glycerin

10	1941.5	1.2671	21.2
20	1923	1.2613	21.7
30	1905	1.2553	22.3
40	1886.5	1.2491	22.8
50	1868.5	1.2427	23.4

Bromoform

10	953	2.886	38.7
20	928	2.858	41.2
30	907	2.830	43.5
40	886	2.802	46.1
50	865	2.774	48.8

Aniline

0	1742	1.0389	32.2
10	1700	1.0303	34.0
20	1659	1.0216	36.1
30	1619	1.0130	38.2
40	1579.5	1.0044	40.5
50	1540	0.9957	42.9

	Vel. of sound, 45°	Vel. of sound, 20°	d^{20}	$\beta\phi$ at 20°, $\text{atm.}^{-1} \times 10^4$
<i>n</i> -Heptane	1048	1154.0	0.6836	111.40
2-Methylhexane	1014	1120.0	.6789	119.05
3-Methylhexane	1033	1135.5	.6870	114.45
3-Ethylpentane	1061	1169.5	.6982	106.15
2,2-Dimethylpentane	972	1080.5	.6737	128.90
2,3-Dimethylpentane	1039	1148.5	.6942	110.70
2,4-Dimethylpentane	984.5	1083.5	.6745	128.00
3,3-Dimethylpentane	1024.5	1129.5	.6935	114.55
2,2,3-Trimethylbutane	1000	1101.5	.6901	121.05
2,2,4-Trimethylpentane	998.5	1098.5	.6918	121.45

TABLE III

COMPARISON OF ISOTHERMAL COMPRESSIBILITIES OF BENZENE AND ETHYL ALCOHOL FROM VARIOUS SOURCES

Temp., °C.	F., H. and A. (1 atm.)	Tyrer 1-2 atm.	Pagliano and Palazzo ^a (1-4 atm.)	Röntgen ^b (8 atm.)	Amagat ^c
Benzene					
17.9	...	...	...	91.7×10^{-8}	...
20	94.9×10^{-6}	95.3×10^{-6}	90.1×10^{-6}	...	...
40	111.0	110.7	105	...	...
Ethyl Alcohol					
0	97.6	99.6	97	...	100×10^{-8} (extrpd.)
10	104.4	106.6	...	...	...
14	...	...	...	...	101
20	111.3	112.9	105.3	...	115 (extrapolated)
40	127.8	128.6	117.8	...	129

^a Pagliano and Palazzo, *Ann. Phys. Chem.*, (iii) **44**, 1 (1891).^b Röntgen, *Mem. accad. Lincei*, (vi) **19**, 30 (1883).^c Amagat, *Ann. chim. phys.*, **29**, 523 (1893).

results of the velocity of sound measurements and the compressibilities and compressibility ratios calculated from them.⁵

The blanks are due to the absence of certain specific heat and coefficient of expansion data. It is hoped to fill these soon by measurements to be undertaken in this Laboratory. The density, specific heat and coefficient of expansion values used were the same as those used by Tyrer,⁶ in the cases where comparison is made of the measured adiabatic compressibility data with those calculated from the velocity of sound. They are believed to be very trustworthy. Those not from this source were taken from the Landolt-Börnstein "Tabellen" and the "International Critical Tables." Table III is given to indicate briefly how the calculated compressibilities compare with those experimentally determined. In Figs. 5 and 6 are shown the velocities of sound and adiabatic compressibilities plotted against temperature. Tyrer's values for the compressibility of ether are included, since the compressibility data from the two sources for this liquid show a greater disagreement than do the data for any of the other liquids.

Attention is called to the slight deviation from linearity of the velocity of sound curve for benzene in a short temperature range just above the melt-

⁵ The following are the equations used

$$V = \sqrt{\frac{1}{\beta_{\varphi}\rho}} \quad \beta_T = \beta_{\varphi} + \frac{\left(\frac{dv}{dT}\right)^2 \rho T}{J C_p} \quad \frac{C_p}{C_v} = \frac{\beta_T}{\beta_{\varphi}}$$

where V is the velocity of sound; β_{φ} is the adiabatic compressibility; β_T is the isothermal compressibility; dv/dT is the differential of the specific volume; J is the mechanical equivalent of heat; ρ is the density; C_p is the specific heat at constant pressure at T° absolute.

⁶ Tyrer, *J. Chem. Sec.*, **103**, 1684 (1913).

ing point. This behavior suggested the measurements on aniline, bromoform, α -bromonaphthalene and glycerin. Except in the case of glycerin, somewhat similar breaks in the curves occur. The glycerin did not freeze.

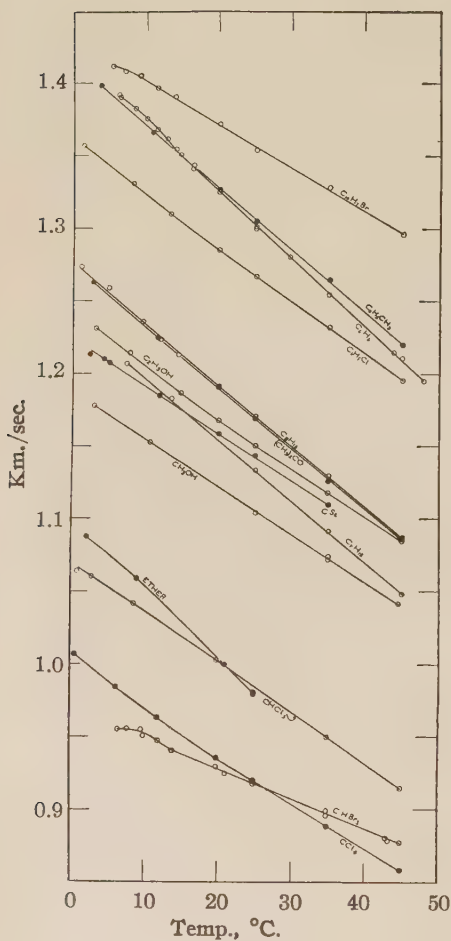


Fig. 5.

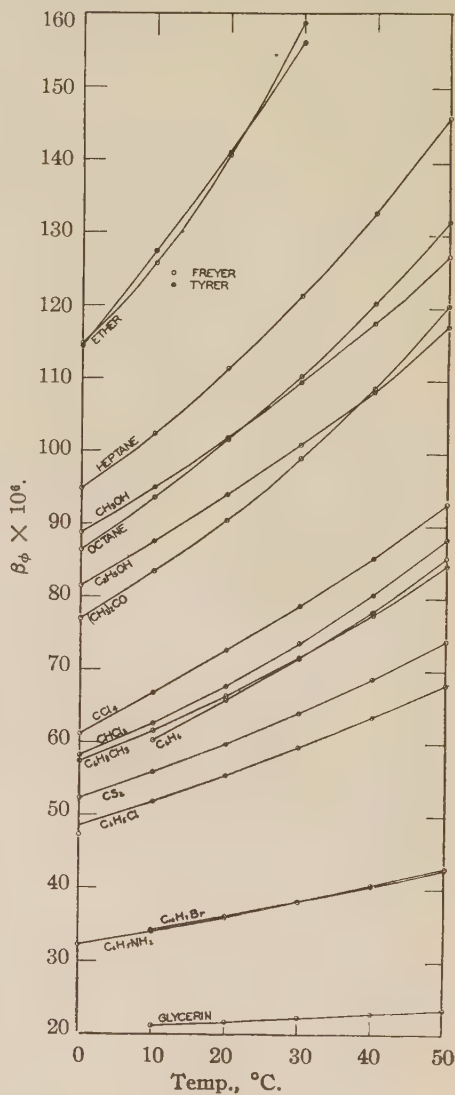


Fig. 6.

It seems reasonable to expect some sort of orientation or grouping of the molecules of liquids to occur preliminary to freezing that would occasion such a change, because the velocity of sound in a liquid is a function of properties directly depending on the molecular arrangement.

Discussing the dipole character of liquids, Gerlach⁷ observes, "Dipoles, by their very nature, are favorable to association—after a fashion—a preliminary stage of microcrystalline character; . . . it is not definitely known whether such a character is in evidence during the solidification of substances like benzol whose molecules exhibit not even the slightest dipole nature. Attention may be directed in this connection to certain experiments of Isnardi in which he has observed variations in the dielectric constant of benzene at temperatures slightly above its crystallization point. This would indicate, under such conditions, the existence of a dipole moment, but since Graffunder's results fail to confirm such a conclusion, further experimental evidence must be awaited." Unfortunately the compressibility measurements of Tyrer⁶ do not cover the temperature range in question in sufficient detail to permit a confirmation of this irregularity in the velocity of sound in benzene by calculation.

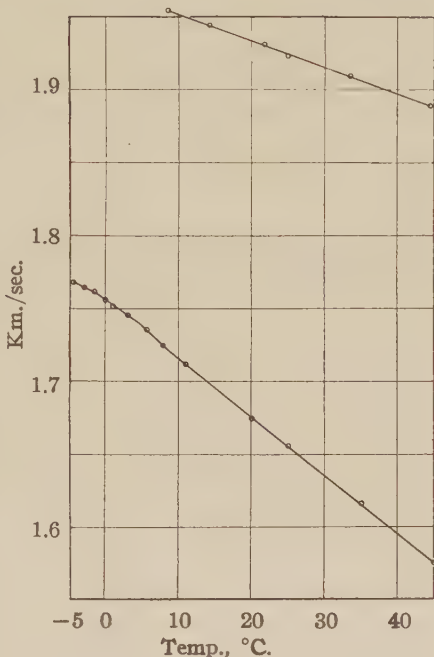


Fig. 7.—Upper curve, glycerin; lower curve, aniline.

The authors are indebted to Mr. Alfred L. Loomis for the use of quartz plates in the interferometer and to the U. S. Naval Research Laboratory for supplying the calibrated quartz frequency control crystal. Grateful acknowledgment is made to Dr. Graham Edgar of the Ethyl Gasoline Corporation for the loan of the isomeric heptanes and for the values of their densities.

Summary

An explanation of the method developed by Hubbard and Loomis for measuring the velocity of sound in small quantities of liquids has been given. The apparatus consists of an electrical oscillator for producing a high frequency field, an oscillator of fixed frequency to control the frequency of the field, and a "sonic interferometer" for producing and determining the wave length of sound waves. The instrument described in this paper is of a new design. The velocity of sound in and the adiabatic

⁷ Gerlach-Fuchs, "Matter, Electricity, Energy" (Translation), 1928, p. 65.

and isothermal compressibility of the following liquids are given: benzene, acetone, ethyl alcohol, methyl alcohol, chlorobenzene, toluene, chloroform, ether, carbon tetrachloride and carbon bisulfide.

The velocity of sound in and the adiabatic compressibility of heptane, octane, aniline, α -bromonaphthalene, glycerin, bromoform and the isomeric heptanes are given.

Some of the compressibility values have been compared with those found by direct measurement by other investigators.

II. THE VELOCITY OF SOUND IN SOLUTIONS OF CERTAIN ALKALI HALIDES AND THEIR COMPRESSIBILITIES

Solutions of Alkali Halides

Since Hubbard and Loomis¹ had observed an apparently anomalous behavior of sodium iodide solutions (compared to those of potassium chloride and sodium chloride) in respect to the course of their curves of velocity of sound against temperature, it was considered desirable to study rather closely the velocity of sound in the chlorides, iodides and bromides of sodium and potassium.

The samples of the salts used were of the "Baker's c. p. Analyzed" grade, the purity of these being sufficiently high for the precision of this investigation. Considering, for example, that the most likely impurity in a given halide of potassium would be the same halide of sodium, it is evident from Fig. 2 that a trace of one salt in the other would have only a very slight effect on the velocity of sound. As much as a tenth of a per cent. of potassium chloride in sodium chloride would lower the velocity of sound in a solution only 0.05 m./sec., and the effect diminishes in the order Cl > Br > I. A precision greater than 1.0 m./sec. is not claimed for these measurements.

Results

In Table I are recorded the same quantities calculated from the velocity of sound as were reported for the organic liquids, except that here the compressibilities, etc., are given as a function of the weight per cent. of salt in solution. The data are for 20°. The density values are from the "International Critical Tables." The coefficients of expansion were calculated from density tables. The specific heat data were taken from the Landolt-Börnstein "Tabellen."

Table II shows (a) the velocity of sound and adiabatic compressibility as a function of temperature for concentrated solutions of the salts, and (b) the velocity of sound alone as a function of both temperature and con-

¹ Hubbard and Loomis, *Phil. Mag.*, [7] 5, 1177 (1928).

centration in the case of the iodides. All these data were taken from smooth curves drawn through the experimental points found by the author and by Hubbard and Loomis, plotted as shown in Figs. 1 and 2. From the first it is seen that increasing the concentration of salt increases the velocity of sound in solutions of sodium chloride, potassium chloride, sodium bromide and potassium bromide. In the case of potassium iodide the velocity decreases and passes through a minimum at about 37%, at 25, 35 and 45°, whereas at 15° the minimum occurs at 20% salt concentration. Considering sodium iodide, the minimum shifts to lower concentration as the temperature is lowered. An explanation of the general course of these curves will be given presently. In Fig. 2 is shown the change in the velocity of sound in solutions of varying concentration as the temperature changes. A characteristic of all the curves is the decrease in slope at a given temperature and a general flattening as the concentration increases. This tendency is least in the case of potassium chloride. The slope of the curve is zero for 45% sodium iodide and becomes negative at higher concentration. Figure 3 shows the lowering of the adiabatic compressibility produced by adding the various salts to water as a function of the quantity of salt added.

Discussion

Since the velocity of sound in a liquid is related to its density and adiabatic compressibility, we should be able to predict changes in the first quantity if we know how the other two vary. The general trend of the velocity of sound-concentration curves is accounted for as follows: the decreasing compressibility tends to increase the velocity, while the increasing density tends to lower it. The predominating effect obviously determines whether addition of salt shall increase or decrease the velocity of sound in the solution. These relations are clearly illustrated by the figures of the first two columns of Table III, where the fractional changes in the compressibility and percentage density change due to adding 10% of each salt are recorded. In the case of sodium chloride the compressibility change greatly predominates and the velocity of sound increases relatively quite rapidly. This predominance decreases in the order $\text{NaCl} > \text{KCl} > \text{NaBr} > \text{KBr}$. The density change has the greater influence in the case of sodium iodide and potassium iodide, and the velocity of sound in solutions of these salts accordingly decreases with concentration. The same reasoning evidently applies also to the curves of Fig. 1, except that here the velocity of sound change is determined by the effect of temperature on the compressibility and density.

Figure 3 shows that a solution of each of the several salts has a lower compressibility than has the pure solvent, and that the lowering produced is greater the larger the amount of salt added. It seemed of interest to examine rather closely the specific effect of each salt at one concentration.

TABLE I
DATA FOR SALT SOLUTIONS

Concn., %	Velocity of sound, m./sec.	ρ	β_ϕ	α	C_p	β_T	C_p/C_v	$\beta_{\phi_0} - \beta_\phi$
NaCl								
1	1497.0	1.0053	45.00×10^{-6}	0.03223	0.986	45.36×10^{-6}	1.008	1.10
6	1554.5	1.0413	40.28	283	.931	40.86	1.014	5.82
10	1600.5	1.0707	36.96	344	.892	37.84	1.024	9.14
16	1673.0	1.1162	32.45	396	.844	33.62	1.036	13.65
20	1722.5	1.1478	29.76	423	.818	31.11	1.045	16.34
24	1771.5	1.1804	27.36	449	.794	28.89	1.056	18.74
NaBr								
1	1487	1.0060	45.56	0.03218	.987	45.90	1.007	0.58
6	1503	1.0462	42.89	276	.932	43.45	1.013	3.21
10	1517	1.0803	40.77	320	.889	41.52	1.018	5.33
16	1541	1.1352	37.60	383	.827	38.70	1.029	8.50
20	1558	1.1745	35.55	421	.788	36.91	1.038	10.55
30	1605	1.2841	30.64	505	.697	32.67	1.066	15.46
NaI								
6	1483	1.0463	44.05	0.03269	.936	44.57	1.012	2.05
10	1483	1.0808	42.64	308	.894	43.33	1.016	3.46
20	1486.5	1.1769	38.97	400	.788	40.19	1.031	7.13
30	1494	1.2907	35.18	477	.688	36.99	1.051	10.92
40	1509	1.4271	31.21	537	.592	33.63	1.078	14.89
45	1524	1.5062	28.97	561	.550	31.66	1.093	17.13
KCl								
1	1492	1.0046	45.32×10^{-6}	0.03215	.985	45.65×10^{-6}	1.007	0.78
6	1530	1.0369	41.76	258	.923	42.25	1.012	4.34
10	1560	1.0633	39.17	287	.877	39.80	1.016	6.93
16	1604	1.1043	35.67	324	.818	36.50	1.023	10.43
20	1633	1.1328	33.55	345	.784	34.50	1.028	12.55
24	1662.5	1.1628	31.55	365	.753	32.63	1.034	14.55
KBr								
1	1486.5	1.0054	45.74	0.03215	.987	46.07	1.007	0.36
6	1495.0	1.0426	43.50	260	.927	44.00	1.011	2.60
10	1502.5	1.0740	41.80	292	.880	42.44	1.015	4.30
20	1521.5	1.1601	37.74	360	.767	38.77	1.027	8.36
30	1545.5	1.2593	33.70	408	.658	35.13	1.042	12.40
40	1573.0	1.3746	29.80	433	.553*	31.55	1.059	16.30
KI								
6	1480.5	1.0437	44.31	0.03257	.932	44.79	1.011	1.79
16	1475	1.1284	41.29	333	.819	42.14	1.021	4.81
30	1472	1.2712	36.80	441	.667	38.24	1.039	9.30
45	1477	1.4672	31.67	462	.512*	33.70	1.063	14.43

To this end a number of properties of the salts and of their ions were sought in the literature, in the hope that a qualitative relation, at least,

TABLE II
EXPERIMENTAL DATA

(a)

Temp., °C.	Velocity of sound, m./sec.	ρ	$\beta\phi$	Temp., °C.	Velocity of sound, m./sec.	ρ
26% NaCl				20% KCl		
20	1796	1.1972	26.25×10^{-6}	15	1623	1.1347
25	1799	1.1944	26.23	20	1633	1.1328
30	1801	1.1917	26.22	25	1641	1.1307
40	1802	1.1861	26.32	30	1649	1.1285
30% NaBr				40	1661	1.1240
15	1599	1.2870	30.80	50	1669	1.1192
20	1605	1.2841	30.64	30% KBr		
25	1609	1.2811	30.56	20	1545.5	1.2593
30	1612	1.2780	30.53	25	1554	1.2566
40	1615	1.2718	30.56	30	1561	1.2539
50	1616	1.2654	30.67	40	1571	1.2484
45% NaI				50	1576	1.2423
10	1525	1.5146	28.77	30% KI		
20	1524	1.5062	28.97	10	1457	1.2762
30	1525	1.4980	29.09	20	1472	1.2712
40	1525	1.4897	29.26	30	1483.5	1.2658
				40	1492	1.2600
				50	1498.5	1.2537
				60	1504	1.2472

(b)

Temp., °C.	KI				Pure water	NaI				
	5%	15%	30%	45%		15%	30.5%	40%	45%	46.8%
15	1465	1464	1465	1473	1467.5	1472	1488	1507	1525	1534
25	1495	1486	1478.5	1481	1498.1	1495	1500	1512	1525	1532
35	1516.5	1503	1488.5	1488	1520.6	1511.5	1508	1515	1525	1530
45	1530	1515	1495.5	1492						1528
55	1538	1522	1501							

TABLE III
DATA FOR 10% SALT SOLUTIONS

	(a) $\frac{\beta\phi_0 - \beta\phi}{\beta\phi_0}$	(b) $\frac{\rho - \rho_0}{0.01 \rho_0}$	(c) γ	(d) $\frac{(b)}{(c)}$	(e) Molecular weight
NaCl	0.198	7.07	0.64	11.1	58.5
KCl	.150	6.33	.58	10.9	74.6
NaBr	.116	8.03	.70	11.4	102.9
KBr	.093	7.39	.61	12.1	119.0
NaI	.075	8.09	.72	11.2	149.9
KI	.065	7.61	.67	11.4	166.0
LiCl		5.59	.93	6.0	
HCl		4.57	1.15	4.0	

might be found between some of these properties and the effect of the ions on the compressibility of their solution. The following question presents itself: what factors may be operative when a salt is added to water that might produce a compressibility change? First, it is conceivable that the presence of ions may change the condition of aggregation of the solvent molecules, *i. e.*, may shift the trihydrol-dihydrol-monohydrol equilibria.

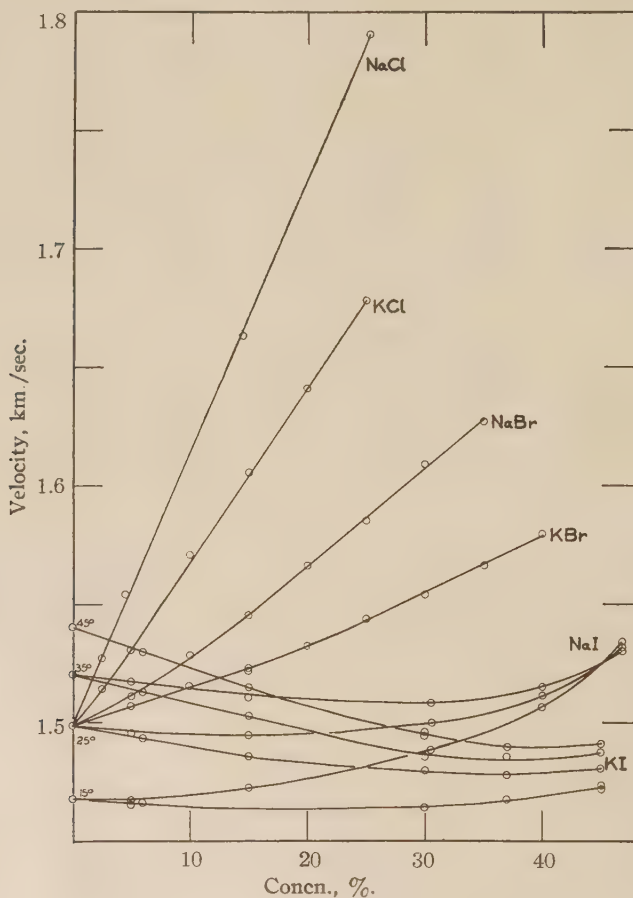


Fig. 1.

Second, it is known that ions concentrate solvent molecules in their immediate vicinity, this hydration being, in effect, a compression, and related to a volume change observed when the components are mixed. It seems a fairly remote possibility that the compressibility of a salt as measured for the solid should have an appreciable effect on that of its solution. The first two possibilities become one when we consider that any effect of the ions on the equilibria between the various hydrols would actually be

brought about as a result of hydration. Now the compressibility of a substance decreases with increasing pressure or, simply, the more a substance is compressed the less it can be compressed. It should accordingly be expected that for a given concentration those solutions will have the lower compressibility whose ions are most hydrated, or, expressed in another way, the lowering of the compressibility produced when different salts are added to water should vary in the same order as the relative degrees of hydration of their ions. Thus Webb² has calculated the contraction of the solvent produced by ions of various radii.

The figures in column two of Table IV represent the mean contraction produced by the two ions composing the salts which affect the fractional compressibility lowerings given in the first column. The assumption is

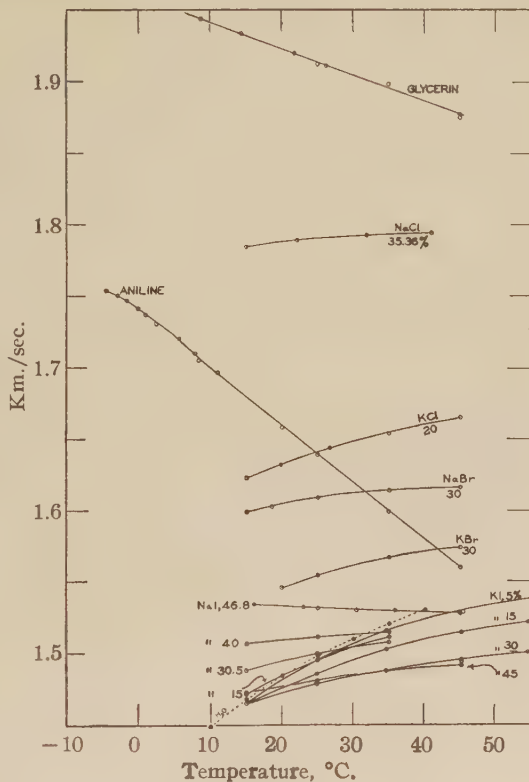


Fig. 2.

made that this contraction effect is a measure of the relative mean degree of hydration of the ions. The third column shows how nearly the compressibility change is proportional to the contraction. The mean ionic radii of the salts as calculated by Webb are given in the fourth column. It is to be noted that in the range considered, the contraction of the solvent is almost inversely proportional to the mean radii of the ions producing it. This is due to the greater intensity of the electric field about the ions of the low atomic number and small radii, resulting in a greater attraction of the water dipoles for the ions. This is the so-called electrostriction.

It would seem desirable, before concluding, to direct attention to one further observation. It is the approximate proportionality between the activity coefficients and percentage density changes due to equal weight percentages of the six salts in solution. This is shown in the last column of

² Webb, *J. Am. Chem. Soc.*, **48**, 2598 (1926).

Table III. The data are for 10% solutions. The relation is seen to be not even approximate in the case of lithium chloride and hydrochloric acid.

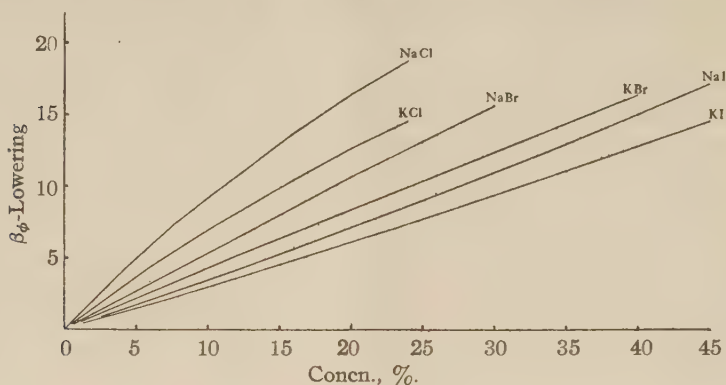


Fig. 3.

This is not surprising in view of the differences in properties usually observed between the elements of the first series of the periodic table and those of the other series. It was found also not to hold for salts of other valence types.

TABLE IV
DATA FOR 3 MOLAL SALT SOLUTIONS

	(a) $\beta\phi_0 - \beta\phi$	(b) Mean relative contraction	(b) (a)	Mean r , Å.
NaCl	0.129	10.7	83	1.87
NaBr	.124	10.2	83	1.95
NaI	.113	9.5	84	2.05
KCl	.116	9.5	82	2.05
KBr	.108	9.0	83	2.12
KI	.105	8.4	80	2.23

Summary

The velocity of sound in solutions of iodides, chlorides and bromides of sodium and potassium has been measured, using high frequencies and a resonance method of detecting nodes. The data cover nearly the entire concentration range for the various salts, and the temperature range 15 to 45°.

The adiabatic and isothermal compressibilities have been calculated for various concentrations at 20°. The adiabatic compressibilities have been calculated as a function of temperature for certain concentrated solutions of the salts.

It is shown that addition of salt lowers the adiabatic compressibility of the solutions, the lowering being quite different for equal percentages of the different salts, and much more nearly equal for equal molalities. In the latter case, the lowering is shown to be related to the contraction of the solvents and hence, presumably, to the hydration produced by the ions

BIOGRAPHY

Egbert B. Freyer was born July 25, 1902, in Marietta, Ga. His primary education was acquired in that city and in Savannah, Ga. He graduated from the Sewanee Military Academy in 1920, and from the University of the South, Sewanee, Tenn., as a Bachelor of Science in 1924. He was a fellow in Chemistry at the University of Virginia during the scholastic year 1924-1925. While there he pursued a research in the field of colloidal chemistry. He received the Master of Science Degree from the Louisiana State University in 1926, where he studied sugar technology. Except for an interval of a few months devoted to industrial work, he has since been a graduate student at the Johns Hopkins University.

